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The Controlled Functionalization of Polystyrene: Introduction of Reactive Groups by Multisite Metalation with Superbase and Reaction with Electrophiles

Lubomir Lockmann, Jean M.J. Fréchet

Department of Chemistry Baker Laboratory Cornell University
Ithaca, New York 14853-1301

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THE CONTROLLED FUNCTIONALIZATION OF POLYSTYRENE: INTRODUCTION OF REACTIVE GROUPS BY MULTISITE METALLATION WITH SUPERBASE AND REACTION WITH ELECTROPHILES

Lubomir Lochmann and Jean M.J. Fréchet *

*Department of Chemistry, Baker Laboratory,
Cornell University, Ithaca, New York 14853-1301, USA*

ABSTRACT

The controlled functionalization of polystyrene using a process of metallation with a potassium superbase followed by reaction with electrophiles is described. The method is advantageous because metallation is extremely efficient occurring rapidly even at room temperature, and the degree of functionalization can be controlled over a very broad range. Functionalization with trimethylsilyl groups allows effective monitoring and quantification of the metallation process. Other examples of modification include the introduction of small dendritic fragments by reaction with a dendron having an aldehydic focal point, or the introduction of carboxylic acid pendant groups. This method which has little effect on the polydispersity of the polymer has broad applicability for the functionalization of a wide spectrum of polymers containing active hydrogens and may also be used to prepare randomly branched or star structures.

INTRODUCTION

A novel approach to the functionalization of polyether dendritic macromolecules¹⁻³ or linear polymers⁴ has been described recently. This method involves metallation of the parent polymer by a superbase (SB) followed by a reaction with an electrophile. The modified superbase prepared from 3-lithiomethylheptane and excess of potassium alkoxide^{5,6} appears to be of particular interest for the metallation of hydrocarbon polymers such as poly(styrene) (PS) because it is fully soluble in aliphatic hydrocarbons. The metallation of poly(styrene) by reagents obtained by complexing butyllithium with polyamines such as tetramethylethylene diamine (TMEDA) has been known for some time⁷⁻⁹ but the kinetics of the process and the degree of metallation are frequently difficult to control. The use of the modified superbase in the metallation of poly(styrene) is now investigated in detail and compared with the metallation with other reagents.

EXPERIMENTAL.

Materials:

Poly(styrene) of molecular weight 20,400 with a polydispersity index $M_w / M_n = 1.04$ was obtained from Pressure Chemical Company. 3-Lithiomethylheptane and potassium tert-pentoxide were prepared according to reference 5 and used to prepare the superbase^{5,6,10}. 3,5-dibenzoyloxybenzaldehyde, [G-1]-CHO, was prepared as previously described¹¹. Organic halides were vacuum distilled in the presence of calcium hydride prior to use. THF was distilled from sodium anthracenide and cyclohexane with butyllithium, both under inert atmosphere. Diazomethane was prepared from DIAZALD (Aldrich Co.).

Characterization of the products:

Proton NMR spectra were recorded in CDCl_3 on a Bruker WM 300 instrument using the solvent signal as internal reference. The size-exclusion chromatography was performed with a Model 510 HPLC pump connected to a U6K injector (Millipore Waters Chromatography) to three 300 mm x 8 mm i.d. PL GEL columns (Mixed C, 100 A and 500 A, Polymer Laboratories) thermostatted at 30°C. The separation was monitored by a differential viscometer (Viscotek Corp.) and a differential refractometer Refractomonitor IV (Milton Roy), column calibration was achieved using 18 polystyrene standards, each injected three times to ensure accuracy of data.

Procedures: Typical procedure for PS metallation and reaction with electrophiles:

A) *Low extent of functionalization* (for concentration of 4 styrene units / SB):

A round bottom flask fitted with a magnetic stirring bar and a three-way stopcock was filled with 10 mL cyclohexane, 5.04 mL 1M solution of potassium tert-pentoxide in cyclohexane (5.04 mmol) and 1.95 mL of 0.863M 3-lithiomethylheptane solution in cyclohexane (1.68 mmol). After 2 min. stirring at room temperature a solution of 0.700g poly(styrene) (6.72 mmol of styrene units) in 15.9 mL cyclohexane was added and stirred for 1 h (final [PS] = 0.20 mol/L). Within a few minutes an orange precipitate, that later became orange-red, separated. Then 0.01 mol of the electrophile was added (deuterium oxide, TMSCl , or dodecyl bromide in the form of a ca. 20% solution in dry THF) to the metallation mixture. Alternatively, an aliquot of the mixture was taken by a syringe, and added to a THF solution of the electrophile. After 15 min. the substituted poly(styrene) was isolated by precipitation in methanol (for the dodecyl derivative 1% LiCl in methanol), the solid was washed with methanol and water, then dried in vacuum at room temperature for 12 hours.

B) *High extent of functionalization*.

For the metallation of poly(styrene) to higher degrees of functionalization the procedure was essentially the same, however, the concentration of poly(styrene) in the final mixture was only 0.15 mol/L. All operations with organometallics were done in an atmosphere of purified argon.

Carboxylated poly(styrene):

The metallation mixture prepared according to the general procedure above was diluted with the same volume of dry hexane and siphoned onto ca. 100g of crushed, dry solid carbon dioxide. After reaching room temperature, the polycarboxylic salt was converted into free acid in the following way: 35 mmol TMSCl was added and refluxed for 2 h under inert atmosphere, then concentrated to ca. 1/3 of the original volume in vacuum (to remove excess of TMSCl), 20 mL water added and refluxed 1 h, then the remaining organic solvent was removed in vacuum. The white solid was filtered off, washed with water and dried in vacuum, dissolved in 20 volumes of THF and precipitated in to 200 volumes of hexane. The free polyacid was filtered, washed and dried in vacuum for 12 h at room temperature. *Esterification of the polyacid:* 0.074g of the polyacid was dissolved in 2 mL THF and a solution of diazomethane in diethylether was added until the evolution of nitrogen ceased and the yellow color of excess diazomethane persisted for 30 minutes. The solution was concentrated to 1/2 of its volume, the polyester was precipitated in hexane and reprecipitated from a THF solution into methanol.

Reaction of polymetallated poly(styrene) with [G-1]-CHO:

To 5.0 mL of the metallation mixture prepared according to the general procedure (containing 1.00 mmol of styrene units with 0.25 mmol of metallated sites) 0.100 g [G-1]-CHO

(3,5-dibenzyloxybenzaldehyde, 0.31 mmol) dissolved in 3 mL THF were added with stirring at room temperature, stirred for 1 h and then 0.5 mL methanol added, giving rise to a yellow solution. The substituted poly(styrene) was isolated from this solution by precipitation into 120 mL hexane with few pieces of solid carbon dioxide (to neutralize the bases). The solid was filtered, washed with hexane and water, dried in vacuum, yielding 0.163g of crude substituted poly(styrene), i.e. 109% mol (impurities). For purification the product was precipitated twice from THF solution in hexane. The higher substituted poly(styrene) (styrene units/SB = 1) was precipitated once more from THF solution into methanol containing 1% LiCl.

RESULTS AND DISCUSSION

Superbase prepared from 3-lithiomethylheptane and three equivalents of potassium tert-pentoxide metallates poly(styrene) smoothly in cyclohexane at room temperature (Scheme 1). The metallated poly(styrene), containing potassium substituents at a multiplicity of sites, separates within few minutes as an orange precipitate. It is likely that this precipitate contains not only the metallated poly(styrene) but also its adduct with the excess of potassium alkoxide. Analogous adducts of potassium alkoxides have previously been described and identified for phenylpotassium¹⁰ and benzylpotassium⁵. The metallation reaction is completed within a few minutes and reaction times longer than 30 min do not appreciably increase the degree of metallation.

Functionalization of metallated polystyrene by reaction with electrophiles.

The "polymetallated" poly(styrene) is then allowed to react *in situ* with various electrophiles to afford a randomly functionalized poly(styrene) within a few minutes of reaction at room temperature. Our initial experiments have used a variety of test electrophiles including the following: deuterium oxide, chlorotrimethylsilane (TMSCl), dodecyl bromide, carbon dioxide and a small dendritic¹¹ aldehyde [G-1]-CHO. In view of the very high reactivity of the organopotassium derivative, it is possible to anticipate favorable functionalization reactions with a broad spectrum of other electrophiles.

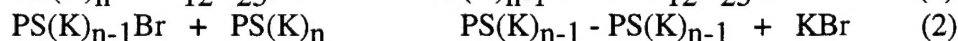
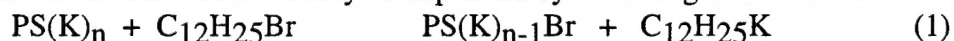
The reaction of polymetallated poly(styrene) with a first generation dendritic aldehyde [G-1]-CHO is not only an example for its reaction with carbonyl compounds, but it also demonstrates the applicability of this grafting process for the preparation of highly branched dendritic structures. An alternative synthesis of this type of copolymers using the direct copolymerization of dendritic macromonomers has been described recently by Hawker and Fréchet¹². A copolymer of dendrimer and poly(styrene) with a reversed architecture may also be prepared in a similar way, i.e. a polyether dendrimer is first metallated by superbase and the metallated dendrimer is then used as a multisite initiator for the anionic polymerization of styrene to finally afford a dendrimer with pendant poly(styrene) chains¹³.

The yields and properties of multisite functionalized poly(styrene) prepared by the method mentioned above using a variety of electrophiles are summarized in Table I. The yields are generally quite high. The degree of poly(styrene) metallation is controlled by the molar ratio of styrene repeat units in the polymer to superbase (PS/SB ratio) and may be varied almost at will within a broad range, such as from 10 to 1 styrene units per equivalent of superbase. The effectiveness of superbase, i.e. the number of functional groups introduced as a function of the amount of superbase used in the metallation, varies from moderate to good (Table I). Lower superbase effectiveness may be caused by the occurrence of side reactions either during the metallation (e.g. superbase decomposition with time) or during the subsequent reaction with electrophiles. In the case of the reaction with the aldehydic dendron [G-1]-CHO, the low

effectiveness may be due to the fact only one equivalent of the aldehyde was used instead of the normal 5 fold excess of electrophile used in other experiments. The results shown in Table I. document that vastly improved results are obtained in the metallation of poly(styrene) with superbase when compared to results obtained with the other reagents previously used for the same purpose⁷⁻⁹. In particular, the kinetics of the metallation reaction appear to much improved with more effective metallation occurring within a shorter time at room temperature. In addition, and as expected, potassium substituted poly(styrene) appears to be significantly more reactive towards electrophiles than its lithium substituted counterpart.

Effect of metallation / functionalization on molecular weight and polydispersity.

In general, the molecular weights of poly(styrene) functionalized by this method are quite close to the calculated values (Table I, Figure 1). The molecular weight distribution data obtained by SEC show that some slight broadening occurs during functionalization, and this tendency is more pronounced if functionalization is carried out to a higher extent. The dodecyl-substituted poly(styrene) is an exception and its behavior is quite unusual (Table I, Figure 1B, curve e). The mean molecular weight of the dodecyl substituted poly(styrene) is much higher than the calculated value, and it exhibits a broad, polymodal molecular weight distribution curve. This behavior may be explained by following side reactions:



As a result of such metal-halogen exchange side reactions that lead to the coupling of polymer chains, molecules with multiples of the original molecular weight are obtained. Thus, even if only a few of these coupling reactions actually occur, they cause a large molecular weight increase while still leaving a significant portion of the metallated sites in poly(styrene) available for the normal nucleophilic displacement reaction on dodecyl bromide. Although the equilibrium in reaction (1) is shifted to the left, even a small amount of metal-halogen exchange has a great effect on the molecular weight distribution of the product because reaction (2) cannot be avoided. As expected, the extent of these side reactions is more pronounced for highly metallated poly(styrene). Interestingly, no crosslinked poly(styrene) has been obtained in this process, obviously because only a very limited number of such coupling reactions occurs.

In contrast to the results obtained with longer metallation times, the polydispersity of substituted poly(styrene) is only slightly higher than that of the starting polymer if the metallation time is kept below 2 hours. For example, the metallation of a narrow dispersity poly(styrene) ($M_w / M_n = 1.04$) for 30 min. followed by protolysis leads to a product with an essentially unchanged polydispersity index ($M_w / M_n = 1.06$). However, if the metallation time is increased to 24 h, the polydispersity index increases to 1.1 (Figure 2, curve (a)). In metallations with no excess of potassium tert-pentoxide (i.e. using a superbase prepared from equimolar amounts of the two components), the increase in polydispersity is significantly higher, reaching a value of 1.2 (Figure 2, curve (b)). This further confirms that it is more advantageous to use modified superbase containing an excess of the potassium alkoxide.

The polymetallated polystyrene is best handled in non-polar hydrocarbon solvents because significant decomposition and other side-reactions occur in the presence of aprotic donor solvents. For example, the polydispersity index of a trimethylsilyl-substituted poly(styrene), prepared by metallation in cyclohexane for 300 min. followed by reaction with chlorotrimethylsilane, is still near 1.09 (Figure 3, curve (a)). However, if the metallation

mixture is diluted with THF and TMEDA (each 20% by vol.) just 10 min. before quenching with TMSCl, the polydispersity index in the final product exceeds 1.6 and a polymodal molecular weight distribution is observed for the reaction product (Figure 3, curve (b)). In addition, the number of organometallic bonds capable of reaction with TMSCl after this treatment decreases and only 0.04 TMS-groups per styrene unit are found instead of 0.2 as is the case in the absence of THF/TMEDA. Thus, donor solvents, especially TMEDA, substantially accelerate the occurrence of decomposition and unfavorable side reactions for potassium multisite-metallated poly(styrene).

Attempts to metallate poly(styrene) under other conditions other than those mentioned above were unsuccessful. The rate of poly(styrene) metallation by a superbases prepared from butyllithium and potassium tert-pentoxide in THF at -80°C was too slow. At room temperature, the reaction of the powerful organometallic reagents with THF predominates. Superbase prepared from butyllithium in cyclohexane is considered to be less suitable for the metallation of poly(styrene) because both the superbases and the metallated poly(styrene) are insoluble in cyclohexane and therefore a slow reaction can be anticipated.

Determination of the site of metallation.

The site of potassium substitution in poly(styrene) was investigated by means of proton NMR spectroscopy using samples quenched with electrophiles and model compounds prepared for comparison purposes. Cumene, used as a simple model for polystyrene, was metallated by superbases using conditions identical to those used for poly(styrene), and the cumylpotassium was then transformed by reaction with TMSCl. Three components were detected by GC/MS analysis in the isolated trimethylsilylated cumene. Two of these (73% by weight) had almost the same mass spectrum and are thought to be isomers of ring substituted cumene. Analysis of the third component (27% by weight) reveals that it is a cumene moiety containing a trimethylsilyl group in its benzylic position. This isomer distribution obtained in this reaction is different from that obtained in the metallation of cumene using the butyllithium-TMEDA complex, where 97% of ring substituted and only 3% of benzyl substituted products were formed¹⁴. The benzylic position in cumene, although thermodynamically preferred, is obviously sterically hindered by the adjacent methyl groups and therefore, side chain metallation is only achieved using the much more reactive superbase. The ^1H NMR spectrum of the mixture of trimethylsilylated cumenes exhibit three resonances of $\text{CH}_3\text{-(Si)}$ protons in the range of -0.5 to 0.5 ppm: at 0.26 and 0.25 ppm (for a total of 87%) and at -0.11 ppm (13%). Although the percentages of substitution determined by the two methods are not in close agreement, the more important finding for subsequent comparisons with substituted poly(styrene) is that TMS-groups bound to aromatic rings absorb around 0.26 ppm, while those bound in the benzylic position absorb upfield at -0.11 ppm.

In another experiment, the polymerization of styrene was initiated by benzylpotassium and then termination of the resulting poly(styrene) was accomplished using TMSCl, giving rise to a poly(styrene) in which each chain has a single TMS-group attached at its terminal secondary benzylic position. The proton NMR spectrum of this polymer exhibits a multiplet between -0.12 and -0.27 ppm. In comparison, the proton NMR spectra of phenyltrimethylsilane^{15a} and benzyltrimethylsilane^{15b} show $\text{CH}_3\text{-(Si)}$ signals at 0.29 and -0.01 ppm, respectively. Thus, it may be concluded that the proton signals for trimethylsilyl-groups bound in the benzylic position of poly(styrene) should be located upfield of 0 ppm.

Two or three signals were detected in the proton NMR spectra of our trimethylsilylated polystyrene in the range between 0.5 and -0.5 ppm, depending on the degree of poly(styrene) substitution. In the "medium" substituted poly(styrene) - with about 5 styrene units/TMS-group - only two major signals at 0.23 and 0.16 ppm are found, corresponding to the ring bound TMS-groups (probably m- and p-derivatives) (Figure 4 A). In addition to the two major signals at 0.2 and 0.16 ppm (representing 85 % of the total TMS substitution), the "highly" substituted poly(styrene) - with about 1.5 styrene units/TMS-group - also shows a new signal at -0.07 ppm (15%) which can be assigned to TMS-groups bound to the backbone benzylic positions (Figure 4 B). It therefore appears that the distribution of regioisomers in the metallation of poly(styrene) depends on the concentration of superbases used for the modification. At higher superbase concentration, some benzylic positions of poly(styrene) can also be metallated in addition to the aromatic rings, while at low superbase concentrations only the aromatic rings are metallated.

Similar findings are also made for poly(styrene) substituted with methoxycarbonyl-group. In a "medium" substituted poly(styrene) (about 4 styrene units/ester group) only two signals near 3.86 ppm were detected (Figure 4 C), while in the "highly" substituted poly(styrene) (about 1.2 styrene units/ester group) signals at 3.86 ppm (80% weight) and near 3.4 ppm (20% weight) were found (Figure 4 D). In comparison, the proton NMR spectra of methyl benzoate^{15c} and methyl phenylacetate^{15d} show CH₃-(O) signals at 3.92 and 3.49 ppm, respectively. Thus, the proton NMR spectra of poly(styrene) substituted with methoxycarbonyl-groups are in full agreement with the spectra of the trimethylsilylated poly(styrene) and confirm a substitution pattern where aromatic substitution predominates over backbone (benzylic) substitution. It is nevertheless interesting to note that the benzylic position, despite its well-known lack of reactivity¹⁶ can actually be accessed.

Overall, these results indicate that the metallation of polystyrene by superbase, and consequently the functionalization by electrophiles, occurs primarily on the aromatic rings of the polymer. The proportion of substituents bound in the benzylic positions of poly(styrene) is low, although it may be increased by using higher SB/PS ratio. Accordingly, our earlier preliminary results on the distribution of substituents⁴ appear to have overestimated benzylic substitution.

CONCLUSION

Superbase appears to be the reagent of choice for the side-chain functionalization of poly(styrene). Randomly substituted poly(styrene)s containing a variety of side-chain pendant groups are obtained in a simple one-pot process involving the introduction of potassium atoms, followed by quenching with electrophilic species. The use of potassium superbases leads to polymers with highly reactive organopotassium sites that are capable of rapid reaction with a broad spectrum of electrophiles. The average degree of substitution of polystyrene may be varied within a broad range and may even reach almost one substituent for each styrene unit. When compared to other metallation procedures, the use of potassium superbases is advantageous for its effectiveness, experimental ease, and applicability to room temperature modifications. Overall, this efficient one-pot procedure, which obviates the need for specialty monomers or demanding polymerization techniques, is likely to be of great interest for the preparation of specialty polymers and copolymers that may have outstanding interfacial properties or high chemical reactivity. The solubility of the superbase in hydrocarbon solvents is also extremely advantageous for the chemical modification of commodity hydrocarbon

polymers such as the newly commercialized high performance elastomers¹⁷ derived from poly(isobutylene-co-4-methylstyrene).

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS.

Figure 1. SEC Eluograms of functionalized poly(styrene)s. Upper part A: (a) unsubstituted PS, (b) deuterated PS (ratio of styrene units per ^2H atom < 2). Lower part B: (b) deuterated PS (ratio of styrene units per ^2H atom < 2), (c) methoxycarbonyl-substituted PS (ratio of styrene units per methoxycarbonyl-group = 1.2), (d) trimethylsilyl-substituted PS (ratio of styrene units per TMS-group = 1.5), (e) dodecyl-substituted PS (ratio of styrene units per C_{12} -group = 1.6)

Figure 2. SEC Eluograms of poly(styrene)s after metallation by various superbases (24 h) and protolysis. (a) Superbase: 2-ethylhexyllithium + 3 equivalents of potassium tert-pentoxide, (b) Superbase: 2-ethylhexyllithium + 1 equivalent of potassium tert-pentoxide.

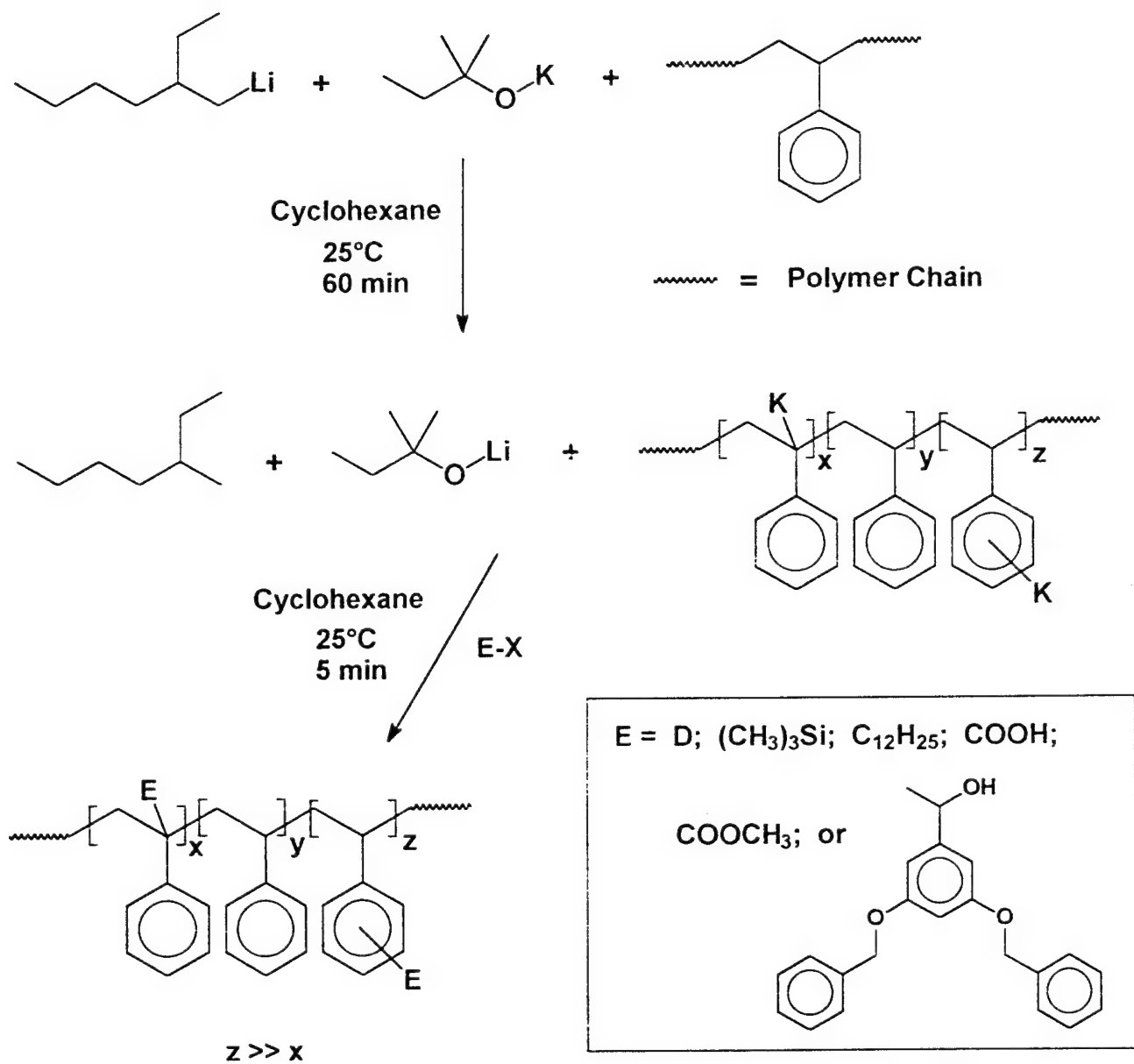
Figure 3. Transformation of multisite metallated poly(styrene) in the absence or presence of aprotic donor solvents. (a) Metallation of poly(styrene) in cyclohexane quenched with trimethylsilylchloride after 300 min. (b) The same metallation mixture quenched with trimethylsilylchloride 10 min. after addition of THF and TMEDA.

Figure 4. Proton NMR spectra of trimethylsilyl- and methoxycarbonyl-substituted poly(styrene)s. (A) 5.3 styrene units per trimethylsilyl-group, (B) 1.5 styrene units per trimethylsilyl-group, (C) 4.1 styrene units per methoxycarbonyl-group, (D) 1.2 styrene units per methoxycarbonyl-group.

TABLE I. PREPARATION OF MULTI-SITE SUBSTITUTED POLY(STYRENE)S

Ratio Styrene Units ^a Superbase	E Group (atom) Introduced	Yield mol%	n (ratio of styrene units / E) ^b	Effectiveness ^c of Substitution %	Mol. Wt. of Substituted PS x 10 ⁻³		
					M _n (calcd.) ^d	M _n (found)	M _w /M _n
4	-D	94	---	---	20.4	21.8	1.11
4	-Si(CH ₃) ₃	93	5.3	75	23.1	29.6	1.08
4	-C ₁₂ H ₂₅	97	6.5	62	25.1	29.4	1.18
4	-COOCH ₃	64	4.1	98	23.2	25.4	1.15
4	-CH(OH)[G-1] ^e	84	6.1	66	30.6	36.4	1.14
1	-D	90	---	---	20.5	19.1	1.09
1	-Si(CH ₃) ₃	91	1.5	6.7	29.8	35.7	1.15
1	-C ₁₂ H ₂₅	75	1.6	61	40.5	60.0	1.86 ^f
1	-COOCH ₃	78	1.2	83	28.0	27.6	1.39
1	-CH(OH)[G-1] ^e	99	2.7	37 ^g	52.4	51.4	1.37

^a Expressed as a molar ratio. The poly(styrene) used had $M_n = 20,400$, $M_w/M_n = 1.03$;^b n is the average number of styrene units per unit of electrophile group E incorporated (calculated from ¹H-NMR data);^c Effectiveness = [styrene units/superbase] 100 / n;^d M_n (calcd) = 196 [104.1 + Mol. Wt. (E) - 1 / n]^e G-1 is a 3,5-dibenzoyloxyphenyl moiety, for structure see lower right hand corner of box in Scheme I;^f The polymer has a broad polymodal molecular weight distribution^g Only one equivalent of aldehyde electrophile was used for this reaction.



SCHEME 1.

Figure 1

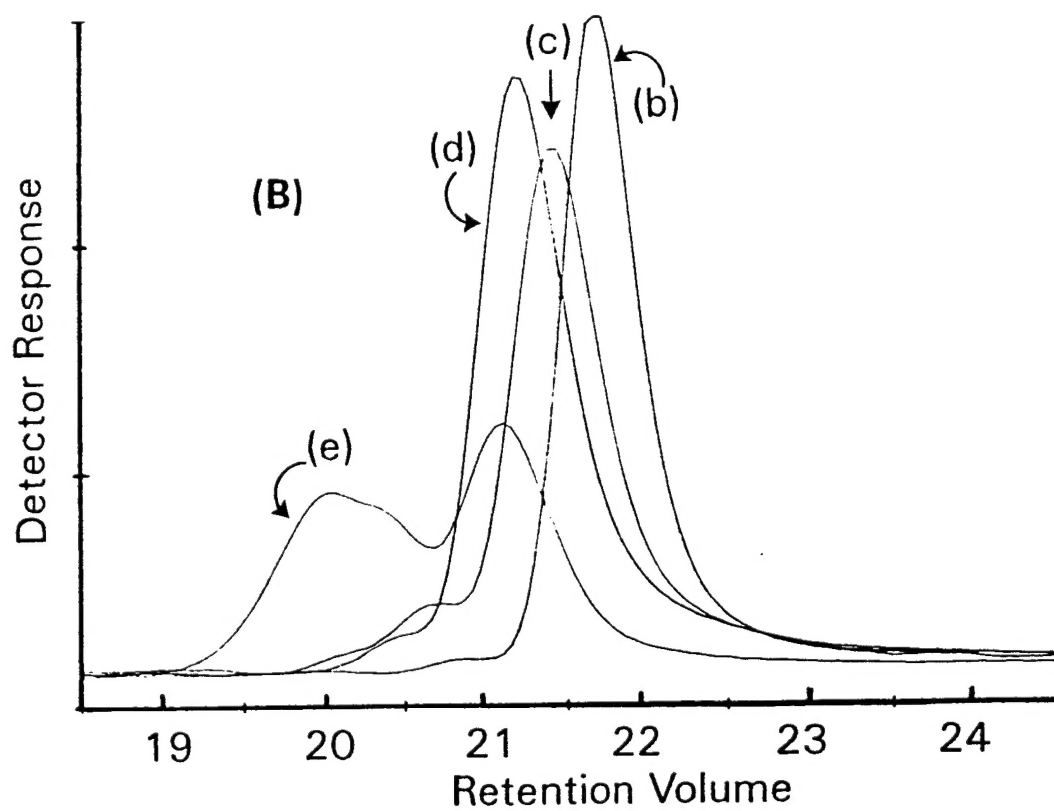
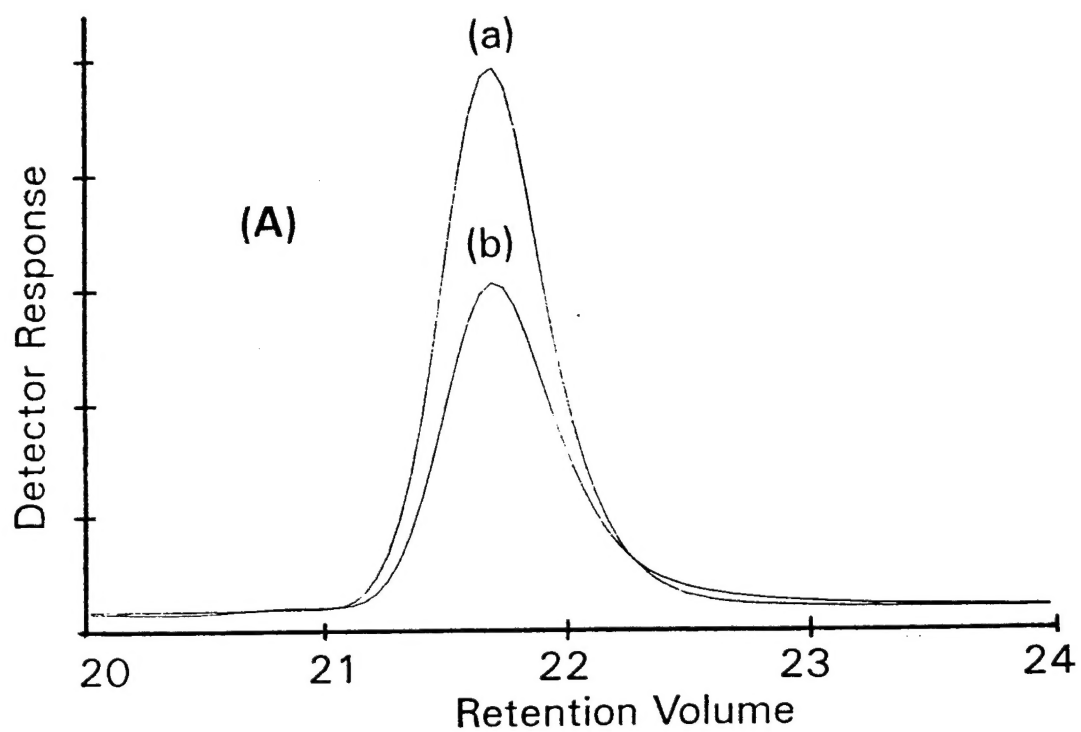


Figure 2

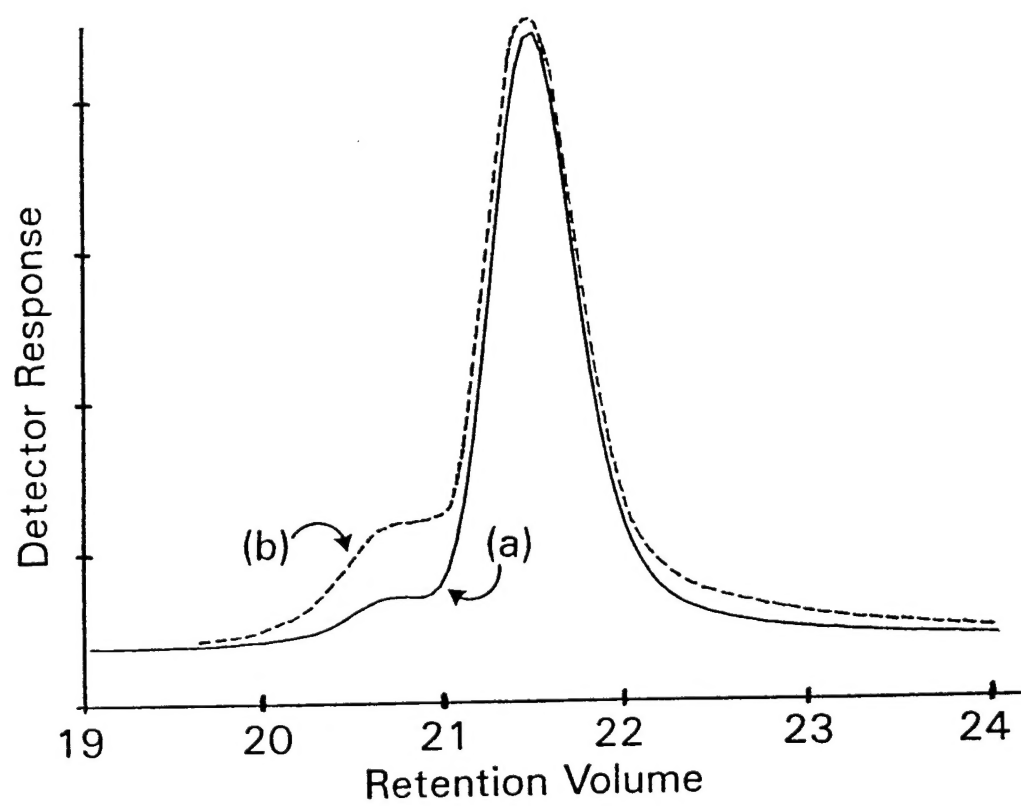


Figure 3

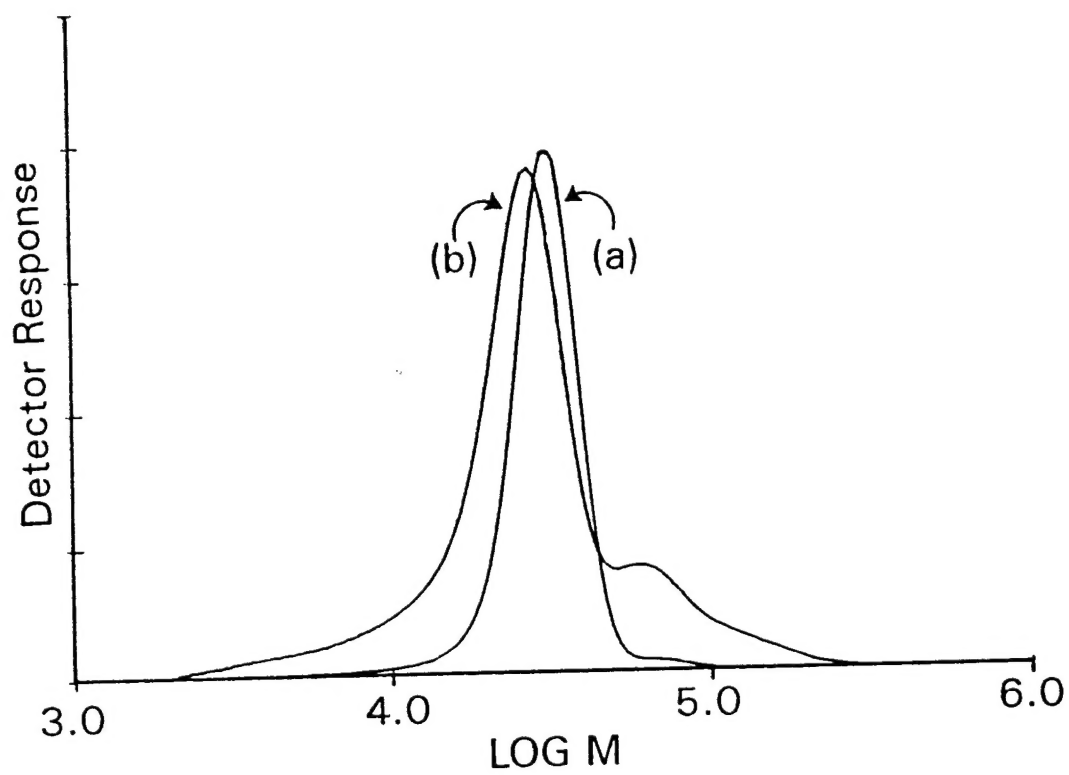


Figure 4

